

**CATALYST FOR AROMATIZATION OF ALKANES,
PROCESS OF MAKING AND USING THEREOF**

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SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION: This invention relates to a catalyst for the aromatization of alkanes to aromatics, specifically a zeolite, preferably a MFI-type structure, most preferably a ZSM-5 MFI
10 zeolite, catalyst for the aromatization of alkanes having two to six carbon atoms per molecule to aromatics, such as benzene, toluene and xylene.

DESCRIPTION OF THE PRIOR ART:

Zeolite is a crystalline hydrated aluminosilicate that may
15 also contain other metals, such as sodium, calcium, barium, and potassium, and that has ion exchange properties (Encarta® World English Dictionary [North American Edition] © & (P) 2001 Microsoft Corporation). A method for preparing a zeolite comprises (a) preparing an aqueous mixture of silicon oxide and sources of
20 oxides of aluminum; and (b) maintaining said aqueous mixture under crystallization conditions until crystals of said zeolite form. Much zeolite research has focused on the synthesis of zeolite frameworks containing elements other than silicon and aluminum.

U.S. Patent no. 6,160,191 discloses that the term "zeolite"
25 includes not only aluminosilicates but substances in which the

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aluminum is replaced by gallium, titanium, iron or boron and substances in which silicon is replaced by germanium, tin and phosphorous. U.S. Pat. Nos. 3,329,480 and 3,329,481, both issued to D. A. Young, report the existence of crystalline
5 zirconosilicate and titanosilicate zeolites. A zeolite having chromium in the tetrahedral positions has been described by Yermolenko et al at the Second Oil Union Conference on Zeolites, Leningrad, 1964, pages 171-8 (published 1965). However, D. W. Breck, in Zeolite Molecular Sieves, p. 322, John Wiley & Sons
10 (1974) suggests that the chromium present was not present in a zeolite A structure and furthermore was present as an impurity in insoluble form. The impurity was said to be in the form of a chromium silicate as confirmed by the nature of the water vapor adsorption isotherm.

15 The zeolite ZSM-5 has been synthesized with many elements other than Al in the framework, including iron. Synthesis of an iron-containing zeolitic structure was reported in Japanese Kokai 59,121,115, published July 13, 1984, which disclosed an aluminosilicate having a faujasite structure and containing
20 coordinated iron. The chemical composition is said to be of the formula $aM_{\frac{1}{n}}O:bFe_2O_3:cSiO_2$, where M can be H, alkali metal or alkaline earth metal; the symbol n is the valence of M; $a=1+/-0.3$; c is between 4.6 and 100; and a is less than b and both are less than 7. The crystal lattice parameter a_0 is between 24.3 and 24.7

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angstroms. Similarly, U.S. Pat. No. 4,208,305 discloses crystalline silicates which are structurally a three-dimensional network of SiO_4^{2-} , FeO_4^{2-} and, optionally, AlO_4^- , GaO_4^- and GeO_4^- tetrahedrons, which are interlinked by common oxygen atoms and are
5 of the overall composition in dehydrated form:

$(1.0 \pm 0.3)(\text{R})_{2/n}\text{O} [a\text{Fe}_2\text{O}_3, b\text{Al}_2\text{O}_3, c\text{Ga}_2\text{O}_3,] y(d\text{SiO}_2, e\text{GeO}_2),$

where R is a cation; $a \geq 0.1$; $b \geq 0$; $c \geq 0$; $a+b+c=1$; $y \geq 10$; $d \geq 0.1$; $e \geq 0$; $d+e=1$; and n is the valence of R. Silicates not containing gallium, germanium and aluminum are preferred. Silicates of a
10 particular X-ray powder diffraction pattern are also preferred.

U.S. Pat. No. 4,713,227 discloses crystalline metalloaluminophosphates having microporosity, catalytic activity and ion-exchange properties which contain metals such as arsenic, bismuth, cobalt, iron, germanium, manganese, vanadium and antimony
15 within the framework.

U.S. Patent no. 5,179,054 states that although matrices may be formed with the germanium analog of silicon, these are expensive and generally no better than the metasilicates, i.e., aluminosilicate, gallosilicate, ferrosilicate and borosilicate,
20 for the molecular sieve component of a catalyst for catalytic cracking of heavy hydrocarbon oils to produce hydrocarbons boiling in the gasoline and distillate range.

In the publication "Aromatization of butane on Pt-Ge

intermetallic compounds supported on HZSM-5" by T. Komatsu et al in Applied Catalysis A: General, vol. 194-195, p. 333-339 (2000) platinum-germanium intermetallic species, platinum species and germanium species were deposited on HZSM-5 for catalysts to
5 convert butane to aromatics. The Pt-Ge intermetallic catalyst was reported to have a more stable time on stream for conversion and selectivity than that of the Pt catalyst. Catalysts with large amount of germanium relative to platinum were reported to have lower conversion of butane and lower selectivity to aromatics.

10 U.S. Patent no. 4,704,494 discloses a process for conversion of low molecular paraffin hydrocarbons to aromatic hydrocarbons using a platinum- or gallium-modified metallosilicate (Si/Me) catalyst where Me is aluminum, gallium, titanium, zirconium, germanium, lanthanum, manganese, chromium, scandium, vanadium,
15 iron, tungsten, molybdenum, nickel or a mixture thereof. The working examples were prepared with Me being aluminum or gallium. No example with germanium was prepared. There was no suggestion to select germanium over any of the other elements or mixtures of elements.

20 U.S. Patent no. 5,456,822 discloses a process for aromatization of hydrocarbons containing two to nine carbon atoms per molecule with a catalyst containing an MFI zeolite having silicon, aluminum and/or gallium in the framework, a matrix, and gallium, a noble metal of the platinum family and a metal selected

from tin, germanium, indium, copper, iron, molybdenum, gallium, thallium, gold, silver, ruthenium, chromium, tungsten and lead deposited on the zeolite. No example with germanium was prepared.

There was no suggestion to select germanium over any of the other
5 elements or mixtures of elements.

U.S. Patent nos. 4,910,357 and 5,124,497 disclose a process for producing monosubstituted monoalkylaromatics from C₈ paraffins using a nonacid platinum-containing catalyst in which the crystalline material contains tin, indium, thallium or lead.
10 These catalysts provided much higher selectivity to aromatics than other platinum catalysts incorporating other elements in the crystalline material, including germanium.

U. S. Patent no. 6,315,892 discloses a process for making a catalyst of a carrier, platinum and germanium wherein the
15 germanium is introduced as an organic compound which is contacted with the precatalyst in the reaction zone.

U.S. Patent no. 5,227,557 discloses a process for the aromatization of hydrocarbons containing 2 to 4 carbon atoms per molecule using an MFI zeolite catalyst containing platinum and one
20 metal chosen from tin, germanium, lead and indium. Both platinum and the additional metal can be introduced on the MFI zeolite by impregnation, exchange or other known methods. The working examples used impregnation for both platinum and the additional metal. Example E contained 0.3% platinum and 0.2% germanium.

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U.S. Patent no. 4,036,741 discloses a process for converting hydrocarbons (including dehydrocyclization of paraffins to aromatics) with an acidic catalyst of a porous carrier material containing halogen along with platinum, cobalt and germanium
5 uniformly dispersed throughout the carrier material which may be a crystalline zeolitic aluminosilicate. The catalyst was tested as a reforming catalyst for a relatively low-octane gasoline fraction under substantially sulfur-free conditions against a catalyst containing platinum and germanium but without cobalt. The results
10 indicated that cobalt was essential for better activity and activity stability.

Some zeolite catalysts containing a Group VIII metal are susceptible to sulfur poisoning. For some platinum catalysts, despite some sensitivity to sulfur, modest amounts of sulfur, such
15 as 10 to 100 ppm, are acceptable and sometimes preferred. A standard sulfurization method that is well known in the art consists in heating in the presence of hydrogen sulfide or a mixture of hydrogen sulfide and hydrogen or nitrogen to a temperature of between 150 and 800°C., preferably between 250 and
20 600°C.

U.S. Patent no. 4,836,336 discloses a process for converting C_6 - C_{12} paraffinic hydrocarbon feed to aromatics using a noble metal low acidity medium pore size zeolite catalyst. The noble metal is

preferably a platinum group metal (platinum, palladium, iridium, osmium, rhodium or ruthenium) and the zeolite is preferably ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48 or Zeolite Beta. The noble metal is modified to its sulfide form by
5 presulfiding the catalyst with H_2S , SO_2 or an organic sulfur compound to increase aromatic selectivity of the catalyst. Germanium is not disclosed as a component of the catalyst.

It would be advantageous to have a zeolite-type catalyst which maintained relatively constant selectivity for conversion of
10 lower alkanes to aromatics, such as benzene, toluene and xylene, over a period of time on stream.

OBJECTS OF THE INVENTION

Accordingly, an object of this invention is to provide an
15 aluminum-silicon-germanium zeolite on which platinum has been deposited, said catalyst having relatively constant selectivity for conversion of lower alkanes to aromatics.

And, an object of this invention is to provide a process for synthesizing a catalyst of an aluminum-silicon-germanium zeolite
20 on which platinum has been deposited.

Also, an object of this invention is to provide a process for the aromatization of hydrocarbons using a catalyst of an aluminum-silicon-germanium zeolite on which platinum has been deposited.

Further, an object of this invention is to provide a process for pretreating a catalyst for aromatization of hydrocarbons of an aluminum-silicon-germanium zeolite on which platinum has been deposited.

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SUMMARY OF THE INVENTION

These and other objects are accomplished by a microporous aluminum-silicon-germanium zeolite on which platinum has been deposited. The catalyst is synthesized by preparing a zeolite
10 containing aluminum, silicon and germanium in the framework, depositing platinum on the zeolite and calcining the zeolite. The zeolite structure may be of MFI, FAU, TON, MFL, VPI, MEL, AEL, AFI, MWW or MOR, but preferably, the zeolite has a MFI structure, more preferably is ZSM-5 MFI zeolite. The catalyst is used in a
15 process for aromatization of alkanes by contacting the microporous aluminum-silicon-germanium zeolite on which platinum has been deposited with at least one alkane at aromatization conditions and recovering the aromatic product.

BRIEF DESCRIPTION OF THE DRAWINGS

20 A more complete appreciation of the invention and many of the attendant advantages thereof will be readily understood by reference to the following detailed description when considered in connection with the accompanying drawings:

Figure 1 is a graph showing the per cent conversion or selectivity of a catalyst of the present invention related to time on stream in minutes.

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DETAILED DESCRIPTION OF THE INVENTION

Depositing platinum on a MFI zeolite catalyst precursor in which germanium has been introduced into the aluminosilicate framework of the zeolite has been found to produce a catalyst that has increased stability with time on stream, i.e., maintains
10 relatively constant selectivity for lower alkanes to aromatics, e.g., alkanes having two to six carbon atoms per molecule to benzene, toluene and xylene.

The zeolite can be prepared by any known method of preparing a MFI structure of aluminum, silicon and germanium. Zeolites are
15 known to be crystallized silicates and include structures of TO_4 tetrahedra, which form a three dimensional network by sharing oxygen atoms where T represents tetravalent silicon and trivalent aluminum. Trivalent elements such as gallium and, more rarely, boron or beryllium may be substituted for the aluminum.

20

Zeolites generally crystallize from an aqueous solution. The typical technique for synthesizing zeolites comprises converting an amorphous gel to zeolite crystals by a hydrothermal process, employing a dissolution/recrystallization mechanism. The reaction medium also contains structuring agents which are

incorporated in the microporous space of the zeolite network during crystallization, thus controlling the construction of the network and assisting to stabilize the structure through the interactions with the zeolite components.

5 As disclosed in U.S. Patent no. 5,246,688, hereby incorporated by reference, MFI zeolites based on silicon oxide and, optionally, the oxides of titanium, germanium, zirconium and/or tin, are produced by (1) heating an aqueous, homogeneous reaction mixture which comprises (a) an $M_{2/n} SiF_6$ complex, wherein M
10 is a cation of valency n, and, optionally, at least one $M_{2/n} T'F_6$ complex, wherein T' is titanium, zirconium, germanium and/or tin, (b) a reagent providing OH ions by hydrothermal decomposition and a structuring agent (c), e.g., a tertiary amine or a quaternary ammonium compound, whereby a zeolite precipitate is formed
15 therein, and (2) separating and calcining such precipitate to eliminate structuring agent from the pores and channels of the resulting zeolite.

Methods of preparation of a MFI zeolite can also be found in U.S. Patent no. 3,702,886 and in J. Phys. Chem, vol. 97, p. 5678-
20 5684 (1993), hereby incorporated by reference.

The silicon/germanium to aluminum atomic ratio (Si-Ge:Al) of the MFI zeolite is preferably greater than 25:1, more preferably in the range from 45:1 to 250:1, and most preferably in the range from 50:1 to 100:1. The silica to germania ratio is present

preferably in the range from 100:1 to 8:1, more preferably in the range from 50:1 to 10:1 and most preferably in the range from 25:1 to 11:1.

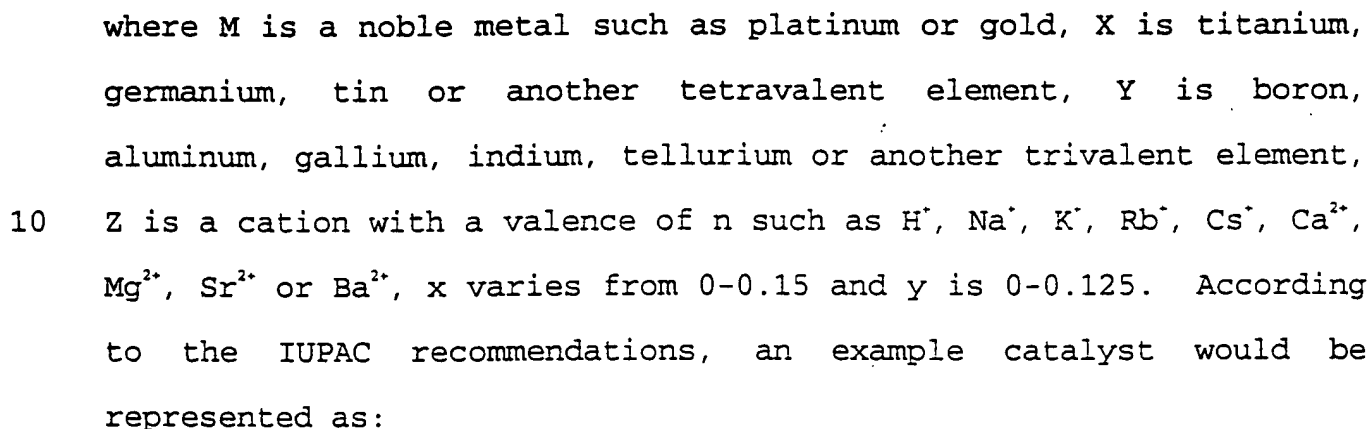
Platinum is deposited on the MFI zeolite by any known method of depositing a metal on a zeolite. Typical methods of depositing a metal on zeolite are ion exchange and impregnation. Platinum is present preferably in the range from 0.05% to 3%, more preferably in the range from 0.2% to 2% and most preferably in the range from 0.2 to 1.5%.

The catalyst may be bound by oxides of magnesium, aluminum, titanium, zirconium, thorium, silicon, boron and mixtures thereof. Preferably, the support is amorphous and is an oxide of aluminum (alumina).

The catalyst preferably has average pore size preferably in the range from 5 angstroms to 100 angstroms, more preferably in the range from 5 angstroms to 50 angstroms and most preferably in the microporous range from 5 angstroms to 20 angstroms.

The catalyst may contain a reaction product, such as platinum sulfide, that is formed by contact of an element or compound deposited on the surface of the catalyst with a sulfur compound. Non-limiting examples of sulfur compounds are H_2S , $C_nH_{2n+2}S$ where $n = 1-20$, $C_nH_{2n+1}S_2$ where $n = 2-22$ and $C_nH_{2n+1}S$ where $n = 2-22$. The sulfur compound may be added before or during the aromatization reactions of light alkanes, i.e., the catalyst may be pretreated with the

5 The chemical formula of the catalyst may be represented as:



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Example 1

ZEOLITE SYNTHESIS:

40.6 g of colloidal silica (40% SiO_2), 2.251 g of aluminum nitrate
[Al (NO_3)₃·9H₂O], 19.575 g of TPAB, 14.7 g of hydrogen fluoride (40%
5 aqueous solution), 91.3 g of methylamine (40% aqueous solution)
and 39.54 g of water were mixed for twenty minutes. 3.93 g of
germanium tetrachloride were added dropwise to the mixture while
stirring. The pH was adjusted to approximately 10 by adding
hydrogen fluoride (40% concentration). The mixture was stirred
10 for 5 minutes. 175 g of the mixture were transferred to an
autoclave reactor and heated at 170°C for eighteen hours. The
resulting solids were washed and dried at 90°C overnight and then
calcined by heating from room temperature to 550°C at 1° per minute
and maintaining the temperature at 550°C for five hours. The final
15 weight of the product was 13.6 g.

FORMING

10.4 g of the zeolite synthesized above was combined with 14.9 g
of hydrated Al_2O_3 and mixed. The mixture was wetted with 0.05N
20 nitric acid to form a dough which was kneaded for fifteen minutes.

The dough was dried overnight at 90°C and then calcined at 550°C
for five hours. The resulting solid was crushed and sieved to
form a 20/40 (U.S. mesh) powder.

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The sieved powder from above was combined with approximately 125 mL of 1.0M ammonium nitrate. The pH was adjusted to 6 with 0.05 N nitric acid. The resulting mixture was placed in an oven at 60°C for one hour, swirling occasionally. The mixture was decanted and the resulting solid was washed for thirty minutes with five aliquots of 60 mL distilled water at 60°C. Optionally, the solid was dried overnight at 90°C.

10 PLATINUM ION EXCHANGE:

1.94 g of $(\text{NH}_4)_2\text{Pt}(\text{NO}_3)_2$ were dissolved in 100 mL of distilled water. 33 mL of the solution was combined with 3 g of the zeolite above. The pH was adjusted to 6 with 0.05 N nitric acid. The mixture was placed in an oven at 60°C for twenty-four hours, swirling every hour for the first four hours. The mixture was decanted and the preceding procedure was repeated twice. The solids were washed five times with 60 mL of distilled water at room temperature for each wash. The solids were dried overnight at 90°C and calcined by heating from room temperature to 300°C at 1°C per minute and maintaining the temperature at 300°C for four hours.

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HYDROGEN SULFIDE PRETREATMENT:

4.003 g of the formed catalyst above was loaded into a reactor, heated to 400°C and swept with 50% hydrogen in nitrogen for four hours. The 50% hydrogen flow was replaced with 1% hydrogen sulfide (20 mL/minute) at 400°C until hydrogen sulfide breakthrough was detected. The hydrogen sulfide stream was replaced with 50% hydrogen in nitrogen (40 mL/min) and treatment continued for one hour at 400°C.

10

COMPARATIVE EXAMPLE A

A zeolite containing only silica and alumina framework elements and a silica/alumina ratio of 150/1 (ZEOLYST CBV 15014G) was formed, ion-exchanged, calcined and pre-treated as in the zeolite synthesis, forming and ion exchanging of Example 1 above.

15

COMPARATIVE EXAMPLE B

15 g of ZSM-5 zeolite containing only silica and alumina (150:1) framework elements was mixed with a finely divided germanium oxide powder (0.30 g). This mixture was then formed, ion-exchanged, calcined, and pre-treated as in the zeolite synthesis, forming and ion exchange in Example 1 above.

20

COMPARATIVE EXAMPLE C

15 g of ZSM-5 zeolite containing only silica and alumina (150:1) framework elements was mixed with a finely divided germanium oxide powder (0.9 g). This mixture was then formed, ion-exchanged, 5 calcined, and pre-treated as in as in the zeolite synthesis, forming and ion exchange in Example 1 above.

CATALYST TESTING:

The catalysts were tested in a stainless steel tube using 15 psia propane diluted with nitrogen to 25 psia total. The weight hourly 10 space velocities (WHSV) were 0.35 to 1.7h⁻¹ depending on the activity of the catalyst employed. The products were analyzed by on-line sampling to a gas chromatograph where all hydrocarbon components with carbon numbers between 1 and 12 were 15 quantitatively determined. Selectivities are expressed on the amount of propane converted; A9+ = C₉-C₁₁ aromatics; BTX = benzene + toluene + xylene.

A catalyst according to Example 1 was tested for propane 20 aromatization and gave the results shown in Table 1. BTX selectivity remained constant for over 100 hours of testing.

Table 1 (Catalyst from Example 1)
WHSV=0.35 h⁻¹; Reaction T = 475°C

Time (h)	Conversion (%)	CH ₄ (wt%)	C ₂ H ₆ (wt%)	C ₄ H ₁₀ (wt%)	A9+ (wt%)	BTX (wt%)
3.5	37	2	24	11	6	56
12.5	34	2	24	13	5	56
24.5	33	2	24	13	4	56
36.5	32	2	24	14	4	55
48.5	33	2	24	14	4	56
60.5	33	2	24	14	3	56
72.5	32	2	24	14	3	56
84.5	31	2	24	14	3	56
96.5	31	2	24	14	3	56
112	30	2	24	14	3	56
137	32	2	23	14	3	57
146	31	2	23	15	3	56

A catalyst according to Comparative Example A was tested for propane aromatization and gave the results shown in Table 2. The selectivity did not remain constant over the first 100 hours.

Table 2 (Catalyst from Comparative Example A)
WHSV=0.35 h⁻¹; Reaction T = 465°C

Time (h)	Conversion (%)	CH ₄ (wt%)	C ₂ H ₆ (wt%)	C ₄ H ₁₀ (wt%)	A9+ (wt%)	BTX (wt%)
3.5	39	2	23	12	8	54
12.5	35	2	26	15	6	50
23	37	2	30	15	6	46
35	38	2	32	16	5	43
47	37	2	33	17	6	41
59	35	2	34	17	5	40
71	37	2	35	18	5	38
83	37	2	36	18	5	38
95	36	2	36	18	5	37
107	35	2	36	19	5	36
119	34	2	36	19	5	36
131	33	2	36	19	5	36
146	33	2	37	19	5	36

A catalyst according to Comparative Example B was tested for propane aromatization and gave the results shown in Table 3. The
5 selectivity did not remain constant.

Table 3 (Catalyst from Comparative Example B)
WHSV=0.6 h⁻¹; Reaction T = 450°C

Time	Conversion	CH ₄	C ₂ H ₆	C ₃ H ₈	A9+	BTX
2	37	2	30	12	6	49
2.75	39	2	31	12	6	49
3.5	38	2	31	12	6	48
4.25	39	2	32	12	5	47
5	38	2	32	12	5	47
9.5	40	2	34	12	5	45
15.5	39	2	35	13	5	44
20	38	2	35	13	5	43
24.5	38	2	36	13	5	43
30.5	37	2	36	13	5	42
35	38	2	36	13	5	42
39.5	37	2	36	13	5	42
45.5	37	2	37	13	5	42
47	37	2	36	13	5	42

10

A catalyst according to Comparative Example C was tested for
15 propane aromatization and gave the results shown in Table 4. The
selectivity did not remain constant.

Table 4 (Catalyst from Comparative Example C)

WHSV=0.3 h⁻¹; Reaction T = 450°C

time	Conversion	CH ₄	C ₂ H ₆	C ₃ H ₈	A9+	BTX
3.2	46	4	42	9	0	45
5.2	46	4	43	10	0	43
9.8	45	4	44	10	0	42
15.2	35	3	41	15	0	41
19.8	35	3	41	15	0	41
25.2	34	3	41	15	0	40
30.5	34	3	42	15	0	40
39.8	34	3	41	15	0	40
49.2	34	3	42	15	0	40
75.2	33	3	42	15	0	40
99.2	33	3	42	15	0	40
125.8	32	3	42	15	0	39
149.2	31	3	42	15	0	39
175.8	31	3	42	15	0	40
199.2	31	3	42	15	0	39
249.2	29	3	41	16	0	39
292.5	28	3	41	16	0	39

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As can be seen from the data above, while the per cent conversion of all of the catalysts are comparable, the catalyst having aluminum-silicon-germanium zeolite on which platinum has been deposited (Example 1) has higher selectivity for benzene-toluene-xylene (BTX) which remained essentially constant for over 100 hours of operation. The catalysts which did not have germanium in the zeolite framework lost effectiveness for BTX selectivity over time.

A catalyst according to the present invention had an X-ray
5 pattern diffraction pattern shown below where given values have
been determined according to standard methods (Radiation: Cu-K-
 α (alpha), Wavelength: 1.54A).

10 Table 5: Main Powder XRD intensities for Ge-ZSM-5

<u>d-spacing[Å]</u>	<u>Intensity</u>
11.15	40
10.04	33
9.77	12
6.38	13
4.27	19
3.85	100
3.77	22
3.72	42
3.66	35

The intensities shown are scaled in arbitrary units so that the
most intense peak is 100. The peaks for Ge-ZSM-5 are shifted
towards higher d-spacing values as compared to an Al-ZSM-5.

15 Numerous modifications and variations of the present
invention are possible in light of the above teachings. It is to
be understood that, within the scope of the appended claims, the
invention may be practiced other than as specifically described.